# APPENDIX

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Chapter IV presented various methods for estimating the volume of free product in the subsurface. The results of seven methods were compared for data representative of the same site conditions. Each of these methods are described in greater detail in this Appendix. To facilitate comparison, a uniform terminology has been adopted. Exhibit A-1 lists the variables that appear in the various equations. Exhibit A-2 is a diagram showing the relationship of the variables and characteristics of free product in the vicinity of a monitor well. Experimental data from Abdul *et al.* (1989) and parameter values for the example calculations are presented in Exhibit A-3.

Exhibit A-1
Variables Appearing in Volume Estimation Equations

β_{ao}	=	air-oil scaling factor
β_{ow}	=	oil-water scaling factor
D	=	function of interfluid displacement pressures and hydrostatics
$\Delta\rho$	=	difference in density between water and hydrocarbon ($\rho_w - \rho_o$)
F	=	formation factor
g	=	acceleration of gravity
h_a	=	distance from water table to bottom of mobile hydrocarbon
$h_{c,dr}$	=	average water capillary height under drainage conditions
H_f	=	thickness of mobile hydrocarbon in the adjacent formation
H_o	=	hydrocarbon thickness measured in the well
P_d^{ow}	=	water-hydrocarbon displacement pressure
P_d^{ao}	=	air-hydrocarbon displacement pressure
ρ_w	=	density of water
ρ_o	=	density of the hydrocarbon liquid
V_o	=	volume of hydrocarbon in the adjacent formation per unit area
ϕ	=	soil porosity
σ_{aw}	=	surface tension of water (= 72 dynes/cm @ 20°C)
σ_{ao}	=	surface tension of hydrocarbon
σ_{ow}	=	hydrocarbon-water interfacial tension (= $\sigma_{aw} - \sigma_{ao}$)
S_r	=	residual saturation
x	=	distance from water table to interface between free product and groundwater in the well-- x is equal to the product of the thickness of the hydrocarbon and the hydrocarbon density ($H_o \cdot \rho_o$)

Exhibit A-2

Relationship of Variables and Characteristics
of Free Product in the Vicinity of a Monitor Well

UST

DTP

H_f

Capillary Fringe

Free Product

H_a

Groundwater Table

H_o

X

Impermeable Layer
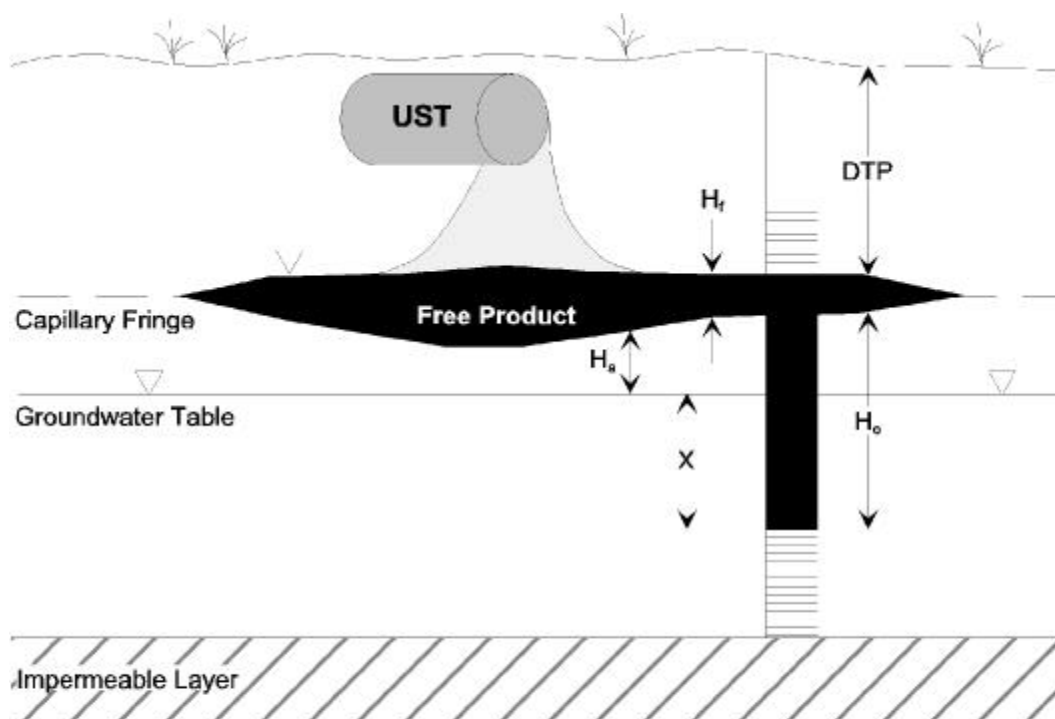
Legend

H_o = apparent (wellbore) product thickness
H_f = actual formation free product thickness
DTP = depth to wellbore product level from ground surface
H_a = free product distance to groundwater table, within formation
X = interface distance below groundwater table, within well

Modified from Ballestero *et al.* (1994).

Parameters and Experimental Data Used
In Calculating Free Product Thickness Based on
Measurements of Free Product in Monitor Wells

Parameters listed in the following table correspond to the variables appearing in the seven equations described previously.

Parameter Values

$\rho_o = 0.84$ gm/cm^3	$\sigma_{aw} = 72$ dynes/cm	$\phi = 0.424$
$\rho_w = 1.00$ gm/cm^3	$\sigma_{ao} = 32$ dynes/cm	$S_r = 0.091$
$F = 7.5$ (med.sand)	$\sigma_{ow} = 40$ dynes/cm	$P_d^{ao} = 5.21$ cm H$_2$O
$h_{c,dr} = 17$	$\beta_{ao} = 2.25$	$P_d^{ow} = 6.51$ cm H$_2$O
$g = 980$ cm/s^2	$\beta_{ow} = 1.80$	$D = 0.035$

The data appearing in the following table are from Abdul *et al.* (1989). Their experiment essentially involved introducing dyed diesel fuel into an acrylic column containing well-graded sand and a minature monitor well. The cylinder was initially filled with water from the bottom and then allowed to drain until equilibrium was reached. Diesel fuel was then allowed to infiltrate from the surface. The height of diesel fuel in the sand and well was measured and recorded. The experiment was repeated 5 times.

Experimental Data

Trial Number	H_o (cm)	h_a (cm)	x [$H_o \cdot \rho_o$] (cm)
1	6	17	5.04
2	63	9	52.92
3	68	6.5	57.12
4	73	2	61.32
5	84	0	70.56

Method of de Pastrovich (1979)

$$H_f \quad \frac{H_o(\rho_w - \rho_o)}{\rho_o}$$

This method depends only upon the density (ρ_o) of the liquid hydrocarbon relative to the density of water. For a hydrocarbon liquid with a density of 0.8, and assuming that the density of water (ρ_w) is equal to 1, the hydrocarbon thickness in the formation (the actual thickness) is only one-fourth the thickness measured in the well (the apparent thickness). Stated another way, the hydrocarbon thickness measured in the well is four times greater than the actual thickness in the formation. The principal weakness of this method is that it does not account for the effects of different soil types. Exhibit III-12 illustrates that in general, the ratio of apparent to true free product thickness increases as soil grain size decreases. Thus, this method may be more accurate in finer grained soil (*e.g.*, silt, clay) than in coarser-grained soil (*e.g.*, sand, loam)

Method of Hall, *et al.* (1984)

$$H_f = H_o - F$$

This method depends upon a "formation factor" (F), which is apparently empirical, and not related to any other type of formation factor (*e.g.*, those found in petroleum literature) (Ballestero *et al.*, 1994). For a fine sand, F is equal to 12.5 cm; for a medium sand, F is equal to 7.5 cm; and for a coarse sand, F is equal to 5 cm. The principal weakness of this method is in selecting an appropriate value for F, especially when the soil is either not one of the three types mentioned above or is layered. Hall *et al.* (1984) also report that there must be a minimum thickness of hydrocarbon in the well for this method to be valid. For a fine sand, the minimum thickness is equal to 23 cm; for a medium sand, the minimum thickness is equal to 15 cm; and for a coarse sand, the minimum thickness is equal to 8 cm.

Method of Blake and Hall (1984)

$$H_f = H_o - (x + h_a)$$

This method is relatively straightforward, depending only upon measured lengths, however, the parameter h_a is difficult to accurately measure especially in the field. Ballestero *et al.* (1994) indicate that h_a should equal the height of the water capillary fringe when the thickness of hydrocarbon in the formation is relatively small since no pore water is displaced. As the thickness of free product builds up, the water capillary fringe becomes depressed as pore water is displaced and the value of h_a diminishes. When the hydrocarbon lens reaches the water table, the value of h_a becomes zero. At this point, the thickness of hydrocarbon in the formation is equal to the distance between the top of the free product layer and the true elevation of the water table. Both of these measurements can be obtained using the methodology illustrated in Exhibit III-10.

Method of Ballestero *et al.* (1994)

$$H_f = ((1 - \rho_o) \cdot H_o) - h_a$$

This method is essentially equivalent to the method of Blake and Hall (1984) when an actual measurement of their parameter "x" is not available, but the product density and thickness of product in the monitor well are known. Recall that x is equal to the product of the thickness of the hydrocarbon in the well and the hydrocarbon density ($H_o \cdot \rho_o$). Rearranging the above equation and substituting x for ($H_o \cdot \rho_o$) yields the same equation. The principal limitation of this method (as well as the method of Blake and Hall) is that the parameter h_a is difficult to measure in the field. When h_a has decreased to zero, the thickness of the free product layer in the soil is equal to the distance between the top of the free product layer measured in the well and the true (corrected) elevation of the water table. Both of these measurements can be obtained using the methodology illustrated in Exhibit III-10.

Method of Schiegg (1985)

$$H_f = H_o - 2(h_{c,dr})$$

This method essentially attempts to correct the exaggerated thickness of free product in a well by subtracting a constant ($2\ h_{c,dr}$) that depends on the soil type. The finer the soil, the greater the constant. Typical values of $h_{c,dr}$, as reported by Bear (1972), are 2-5 cm for coarse sand, 12-35 cm for medium sand, and 35-70 for fine sand. The principal weakness of this method is that it relies on a parameter that is difficult to accurately determine. Values for $h_{c,dr}$ vary by a factor of 2 over the range from low to high. Also, it is possible for this method to yield a negative value if there is only a thin layer of free product in the well.

Method of Farr *et al*. (1990)

$$V_o = \phi(1 - S_r)\ D\ [(\frac{H_o}{D}) - 1]$$

$$D = \frac{P_d^{ow}}{\Delta\rho g} - \frac{P_d^{ao}}{\rho_o g}$$

This method is dependent upon conditions of static equilibrium. Farr *et al*. (1990) present several variations of this equation for different soil types and different extent of liquid hydrocarbon in the unsaturated zone. The above equation is based on equation #15 in their paper, which is valid for unconsolidated sand with very uniform pore sizes. The principal limitation of this method is in obtaining values for P_d^{ow} and P_d^{ao}, neither of which is easily measured in the field. Ballestero *et al*. (1994) present and discuss this method, however there is a discrepancy in the formulation of the "D" term, which is not possible to resolve based on the information provided. Ballestero *et al*. (1994) also mistakenly assume that H_f and V_o are equivalent. The relationship between H_f and V_o is discussed later in this Appendix.

Method of Lenhard and Parker (1990)

$$H_f = \frac{\rho_o \, \beta_{ao} \, H_o}{\beta_{ao} \, \rho_o - \beta_{ow}(1 - \rho_o)}$$

$$\beta_{ao} = \frac{\sigma_{aw}}{\sigma_{ao}}$$

$$\beta_{ow} = \frac{\sigma_{aw}}{\sigma_{ow}}$$

This method is dependent upon conditions of static equilibrium; it assumes a theoretical, vertical saturation profile based on generalized capillary pressure relationships. Extensions of this method allow consideration of residual oil trapped above and below the mobile zone by a fluctuating water table. The principal limitations of this method are that it does not account for dynamic conditions or small-scale heterogeneities, and few of the parameters can be measured in the field. Parameters from published literature for pure compounds may be substituted but it is uncertain how applicable such values are to aged mixtures of petroleum hydrocarbons in the subsurface.

Relationship Between V_o and H_f

Although both the thickness of hydrocarbon in the soil (H_f) and specific oil volume (V_o) can be expressed in dimensions of length [L], they are not equivalent terms. Vertical integration of the hydrocarbon content in the soil yields the volume (V_o) of hydrocarbon in the medium per unit area, whereas H_f is merely the corrected thickness of the free product layer in the geologic formation. V_o actually has dimensions of L^3/L^2 and is commonly expressed in terms of cubic feet per square foot. To determine H_f, V_o must be divided by the effective porosity. In the unsaturated zone, effective porosity is equal to the product of porosity [ϕ] times the quantity 'one minus the residual saturation' ($1-S_r$). The length dimension of the V_o term

is equivalent to the height that a specified volume of liquid hydrocarbon would rise in an empty box measuring one unit of length on each side. The length dimension of the H_f term is equivalent to the height that the same specified volume of liquid hydrocarbon would rise in the same box filled with a porous media (*e.g.*, sand) of porosity ϕ and residual saturation S_r. Obviously, the height of the rise in the box filled with a porous media would be higher than in the empty box. To illustrate this point, consider an empty box that measures one unit of length on each side. Take a specific volume of liquid and pour it into the box. The depth of liquid in the box is equivalent to the specific volume of the liquid. Now consider the same box but this time it is filled with marbles that are packed so that the pore spaces represent only 25 percent of the total volume. If the same volume of liquid is poured into this box, the height of the liquid will be four times greater than the height in the empty box.

Relevance To Free Product Recovery

Each of the above methods for determining volume of free product has its strengths and weaknesses. In general, none of the methods is particularly reliable under any given set of conditions either in the field or in the laboratory. Although there have been some creative attempts to compensate for the limitations of some of the methods, it is not usually possible to predict the accuracy. For example, Huntley *et al*. (1992) apply the methods of Farr *et al*. (1990) and Lenhard and Parker (1990) to a stratified system, with each layer represented by its own specific capillary pressure-saturation curves. The profiles generated by the layered model match measured hydrocarbon saturations better than the use of a single "average" layer. However, the study indicates that predicted saturations can be erroneous if the system is not in equilibrium, and hence in violation of the assumption of hydrostatic pressure distribution. These non-equilibrium effects can be caused by rising or falling water table elevations. Unfortunately, like anisotropy, non-equilibrium is most often the rule, and isotropy and equilibrium are the exceptions. To estimate the volume of free product in the subsurface, no one method should be relied on exclusively. Select the methods that are most appropriate to the site conditions and determine a volume using each method. In this way a reasonable range of values can be established.